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Ozone Treatment of Cyanide-Bearing Plating Waste

Sealectro Corp, West Caldwell, N J

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The use of ozone for CN destruction in the metal finishing industry has long been recognized as a technically attractive alternative to chlorine oxidation. High capital cost has, in earlier years, prevented its implementation.

This report documents a full scale installation in which it was demonstrated that alkaline cyanide waste could be effectively destroyed to levels well below 1 ppm and with CN^- removals of 99% at the levels normally encountered, thus satisfying BATEA requirements. Design features, problems and capital and operating cost data are presented and discussed.

Selected aspects of the cyanide-ozone reaction were also studied, such as the effect of CN^-/O_3 ratios, cyanide source and concentration and the effectiveness of ozone for cyanate elimination.

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OZONE TREATMENT OF CYANIDE-BEARING PLATING WASTE

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This full scale demonstration of a highly automated ozonation system for the destruction of cyanide in electroplating wastewaters will help to establish the technical and economic feasibility of this alternate technology. Such information will be of value both to EPA and to the industry itself. Within EPA's R&D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to cyanide wastes from electroplating, this technology may find application in the control of cyanide from other sources as well as for the destruction of carbonaceous pollutants generated by a host of other industries.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

David G. Stephan
Director
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ABSTRACT

A plating waste treatment plant was built to demonstrate the effectiveness of ozone treatment for the oxidative destruction of cyanides and cyanates and for the removal of copper and silver as their oxides on a plant scale. The plant was designed to treat all the waste from copper, gold, and silver plating operations.

A 9-month study was carried out to evaluate the effect of process parameters, to identify and optimize key parameters, to establish capital cost and operating costs, and to explore the possibility of producing an effluent of the highest quality.

The results of the study clearly show that ozone treatment rapidly and economically destroys copper and sodium cyanides. The reaction first produces cyanates, which are oxidized further by ozone and simultaneously, but much more slowly, hydrolysed. Although the complete removal of cyanates was demonstrated, it was not practiced under optimum conditions since it is not required under local or Federal standards. The process precipitates copper and silver in a readily settleable form. The oxidation of copper cyanide is more rapid and requires less ozone than that of sodium cyanide.

Cost data have been developed to reflect the optimum operating conditions found experimentally. The plant treats a combined cyanide (alkaline) and heavy metal (acidic) flow of 185,000 l/day (49,000 gal/day). The costs of treatment are as follows:

operating cost	$ 0.37/1,000 l ($1.03/1,000 gal)
total cost	$ 0.55/1,000 l ($1.51/1,000 gal)

The costs of ozone treatment of the cyanide waste alone are as follows:

operating cost	$ 0.38/1,000 l ($1.45/1,000 gal)
total cost	$ 0.62/1,000 l ($2.35/1,000 gal)
	$10.34/kg CN ($4.70/lb CN)

Capital investment for this optimized system is estimated as $51,200.

This report was submitted in fulfillment of Demonstration Grant #S802335 by Sealectro Corp. under the partial sponsorship of the U.S. Environmental Protection Agency. Work carried out by PCI Ozone Corp. under contract to Sealectro Corp. covers the period April 1, 1973 to June 30, 1974 and the project was completed January 31, 1975.

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Credit is due to Mr. Charles Baiint (PCI) for the operation of the treatment plant during the study program and to Mr. Barry Siegel (PCI) for the analysis of the samples.

SECTION 1

INTRODUCTION

The electroplating industry produces substantial quantities of wastewater containing cyanide and heavy metals salts. The untreated metal plating waste introduces quantities of toxic pollutants into our streams and rivers, either directly or by exerting a deleterious effect on the operation of sewage treatment systems that receive that waste. To alleviate this problem, economical, simple to operate, effective treatment processes such as ozonation are necessary.

Cyanide wastewater is traditionally treated by chemical means such as oxidation with gaseous chlorine, oxidation with hypochlorites, or precipitation with ferrous sulfate. The ozone destruction of cyanide waste is an additional promising method. This process has not been used extensively in the past primarily because of the relatively high cost of ozone generating equipment. However, significant advances have been made in recent years in the manufacturing of ozone generating equipment, making the cost of ozonation competitive with other processes.

REVIEW OF OZONE DESTRUCTION OF CYANIDE WASTE

The destruction of cyanide in wastewater by ozone is rapid and effective. The process does not require storage of toxic materials. Ozone is generated on-site as needed. The process lends itself to automation. It produces no undesirable salts and leaves the effluent saturated with oxygen (5,6).

A large industrial plant in Wichita, Kansas treats cyanide-containing industrial waste using more than 160 kg (350 lbs) of ozone per day (7). Pilot plant studies followed by a full scale installation in France at 340 l/min (88 gpm) showed that 25 ppm of cyanide can be effectively and economically treated with 80 ppm of ozone. The ozone dosage required per kilogram of cyanide treated decreases with increasing cyanide concentration and with increasing ozone concentration (8,9). It has generally been assumed that 1 to 1.5 parts of ozone oxidizes one part cyanide (CN^-) to cyanate and up to 3.5 parts are needed to carry the oxidative treatment beyond the cyanate state, probably to carbon dioxide and nitrogen. Cyanate also hydrolyses slowly during treatment.

Several laboratory studies have been carried out focusing on various aspects of cyanide wastewater treatment by ozonation (10-21). The results of

some of these studies appear to be contradictory because the experiments were carried out under different, non-comparable reaction conditions. Nevertheless, it is clear from such studies that mass transfer of ozone from air to water controls the reaction rate in most cases (11,12). In a batch reactor study, the pH of the solution changes drastically during ozonation, first decreasing to an acidic pH, then increasing to a basic pH again as the oxidation of cyanide progresses through cyanate and then to what was believed to be urea and ammonium nitrate (11). More recent work (11b) projects that the products are carbon dioxide and nitrogen. Certain metal salts, such as those of copper, appear to catalyse the oxidation reaction when mass transfer is not the limiting factor (12). The oxidation of certain hard-to-oxidize complexes of cyanide such as sodium ferricyanide is accelerated by ultraviolet (uv) irradiation, heating to 93°C (100°F) or both (31).

The stoichiometry of the reaction has been studied under two sets of different reaction conditions (11,12). From these studies, it appears that the number of moles of ozone required for the destruction of one mole of cyanide is dependent on cyanide concentration, on ozone concentration and on pH. These findings suggest the presence of competing side reactions. In general, higher cyanide concentrations, higher ozone concentrations, and higher rates of ozone mass transfer favor lower ozone dosage for cyanide destruction.

Oxidation-reduction potential measurements (ORP) were found to be a good indication of the progress of the ozone/cyanide reaction (11).

A laboratory study preceding this demonstration project clearly established that the oxidation of cyanides by ozone destroys both cyanides and cyanates. That is, the reaction does not stop at the cyanate stage. Furthermore, the ozone treatment precipitates copper and silver as a dense, readily filterable or settleable precipitate which is believed to be composed primarily of the metallic oxides (6).

THE PLATING OPERATION AT SEALECTRO CORPORATION

Sealectro Corp., a manufacturer of connectors and other related components for the electronics industry, decided to build a new plating plant to satisfy its requirements internally in the gold, silver, copper and nickel plating area. The plant was designed in-house and installed by Sealectro's maintenance personnel.

The expected wastewater flows from the plant, based on design, were as follows:

a) Alkaline cyanide flow: 25.5 l/min (6.75 gpm) with surges to 39.0 l/min (10.4 gpm) containing contaminants in the following maximum concentrations (mg/l):

cyanide.....60
copper.....31
silver..... 3.4

b) Acidic wastewater flow: 60 l/min (16 gpm) with surges to 93.0 l/min containing contaminants in the following maximum concentrations (mg/l):

nickel	14
tin	2
lead	0.08

In order to be discharged, the treated effluent had to meet or exceed the requirements of Act. No. 37-1968, County Public Works Sewer Ordinance No. 1, Board of Supervisors of Westchester County, N.Y., effective May 20, 1968, which may be summarized as follows:

1. pH in the range of 5.5 to 9.5
2. temperature not to exceed 65°C (150°F),
3. maximum concentration of toxic substances (mg/l):

copper	3.0
cyanate	10.0
cyanide	1.6
nickel	10.0
silver	0.05
chlorine	100.0

After the construction of the Sealectro Plating Waste Treatment Plant, the EPA published guidelines and standards on March 28, 1974 (Federal Register, Vol. 39, No. 61, covering the waste treatment requirements for the plating industry). The permissible amounts of pollutants are related to the surface area plated as summarized in Table 1.

TABLE 1. PLATING WASTE EFFLUENT LIMITATIONS

Best Practicable Technology Currently Available, 07/01/77

Parameter	Effluent (mg/m²)	
	1 day max.	30 day avg. max.
Cu	160	80
Ni	160	80
Cr (VI)	16	8
Cr, total	160	80
Zn	160	80
CN,A*	16	8
CN, total	160	80
TSS	4800	3200
pH	6.0-9.5	6.0-9.5

*CN, A means chlorine-oxidizable cyanides.

A monthly average rinse water flow of 80 l/m^2 (1.96 gal/ft^2) of plated surface is assumed with a one day maximum of 160 l/m^2 (3.93 gal/ft^2). On the basis of 80 l/m^2 (1.96 gal/ft^2) the concentrations of contaminants permitted were calculated as shown in Table 2 for BPTA.

TABLE 2. MONTHLY AVERAGE CONCENTRATIONS OF CONTAMINANTS*

Pollutant	BPTCA Effluent Parameters (mg/l)
Cyanide (Dest. by Cl)	0.1
Total	1.0
Copper	1.0
Iron	2.0
Lead	1.0
Nickel	1.0
Silver	0.1
Tin	2.0
Zinc	1.0
TSS	40.0
pH (avg. Daily Discharge)	6.0-9.5

*Based on 80 l/m^2 flow and 30 day average maximum discharge rates.

SECTION 8

CONCLUSIONS

The Sealectro demonstration project achieved its major objectives. It has demonstrated on a plant scale the effectiveness of ozone for cyanide and cyanide-bearing plating waste treatment. It has confirmed the results of laboratory work in the laboratories of PCI Ozone Corp. in Stamford, Connecticut* concerning the removal of cyanide, cyanate, copper, and silver by ozone treatment.

The major results of the study may be summarized as follows:

a) Optimum operating conditions were determined for the Sealectro Plant to be 1 to 1.5 moles of ozone/mole CN^- at a pH of 7 to 9.5 in the ozone contactor and a final clarifier pH of 9 to 9.5 at ambient temperatures of 14 to 20°C (57 to 68°F).

b) It was established that the ozone dosage is the most critical operating parameter, with 1 to 1.5 moles O_3/mole CN^- found to be optimum at low CN^- concentrations ($\leq$ 20 mg/l) and 1.8 to 2.8 moles O_3/mole CN^- at higher levels ($\geq$ 40 mg/l).

c) The pH of the cyanide waste in the ozone contact tank was found to have no significant effect in the range of 7 to 10, thereby eliminating the need for precise pH control during ozone treatment.

d) Firm cost data were established based on plant experience. Treatment operating cost was $0.58/1000 liters ($1.45/1000 gal) of CN^- influent and $0.27/1000 liters ($1.05/1000 gal) total wastewater. The total capital costs were $66,613.00 for the Sealectro installation but are estimated at $51,200 for an optimized, non-research installation.

e) The ozone treatment proved to be a safe operation. It did not emit ozone into the atmosphere.

f) Side benefits of ozone treatment include improved safety by eliminating the need for the transportation and storage of toxic and hazardous chlorine or hypochlorite and, in general, a sophisticated and highly automated operation requiring a minimum of attention and chemical additions.

*Now located in West Caldwell, N. J.

SECTION 5

RECOMMENDATIONS

The Sealectro demonstration project achieved its major objectives and clearly demonstrated that ozone treatment is an effective, economical and safe method for cyanide plating waste treatment. We recommend a further demonstration study covering the following areas.

Recycling of treated effluent into the plating process should be possible by providing a small increase in ozone dosage, eliminating cyanide from the acid flow* and improving the operation of the settling tank. The effluent is suitable as is for the cooling of operating machinery, such as ozone generators, air conditioners, etc.

Other metal complexes of cyanide should also be responsive to ozone treatment. These metal complexes include those of cadmium, zinc, and iron. (The removal of the iron complex, a particularly stable one, may require simultaneous ultraviolet irradiation or elevated temperatures).

The severity of treatment conditions should be determined for each metal complex anticipated in a plating plant.

* Cyanide was discovered in the acid stream of the Sealectro Plating Plant and ultimately found to be due to plumbing and maintenance difficulties. The problem was only partially resolved during the course of the study program.

SECTION 4

DESIGN OF TREATMENT PLANT

The plating wastewater treatment plant was designed and installed by PCI Ozone Corp. under the direction of Dr. L. J. Bailyky. It was started up in January 1974, placed into full operation February 25, 1974 and has been in operation since that date with no design or operation-related downtime.

The Sealectro Plating Waste Treatment Plant is designed to treat the two wastewater streams produced during the plating operations of the Sealectro Corp. Plating Plant. The expected discharges from the plating plant are as follows:

Alkaline cyanide wastewater: Flow under normal conditions, 25.5 l/min (6.75 gpm), with provision to accept surges in flow (spills, bath discharges, etc.) or growth to 39 l/min (10.4 gpm). The wastewater contains cyanide up to 60 mg/l, copper up to 32 mg/l, silver up to 3.4 mg/l.

Acid waste: Flow under normal conditions, 60 l/min (16 gpm), with provision to accept surges in the flow or growth to 93 l/min (24.6 gpm). This flow may contain nickel up to 14 mg/l, tin up to 10 mg/l, and lead up to .08 mg/l concentrations.

The combined average flow of acid and cyanide waste is 86 l/min (22.75 gpm), with provisions to accept surges in flow rates up to a total of 132 l/min (35 gpm) flow. Peaks and surges are to be equalized in separate underground holding tanks.

The plant is designed to operate continuously around the clock, if necessary. The flow of both wastewater streams is controlled automatically, as is the pH of the cyanide stream and of the effluent from the treatment plant. The ozone dosing rate is also controlled automatically by on-line monitoring of residual ozone.

Flexibility was engineered into the plant and numerous sampling points were provided to allow for experimentation and modifications necessary for the demonstration study. Thus, this plant is over-designed to allow variation of process parameters over a broad range.

The general design of this wastewater treatment plant is shown in the flow diagram, Figure 1. The plant has two separate underground storage tanks to receive and equalize the segregated wastewaters; a 7500 l (2000 gal) tank for the alkaline cyanide waste (T-2), and a 15,000 l (4000 gal) tank for the

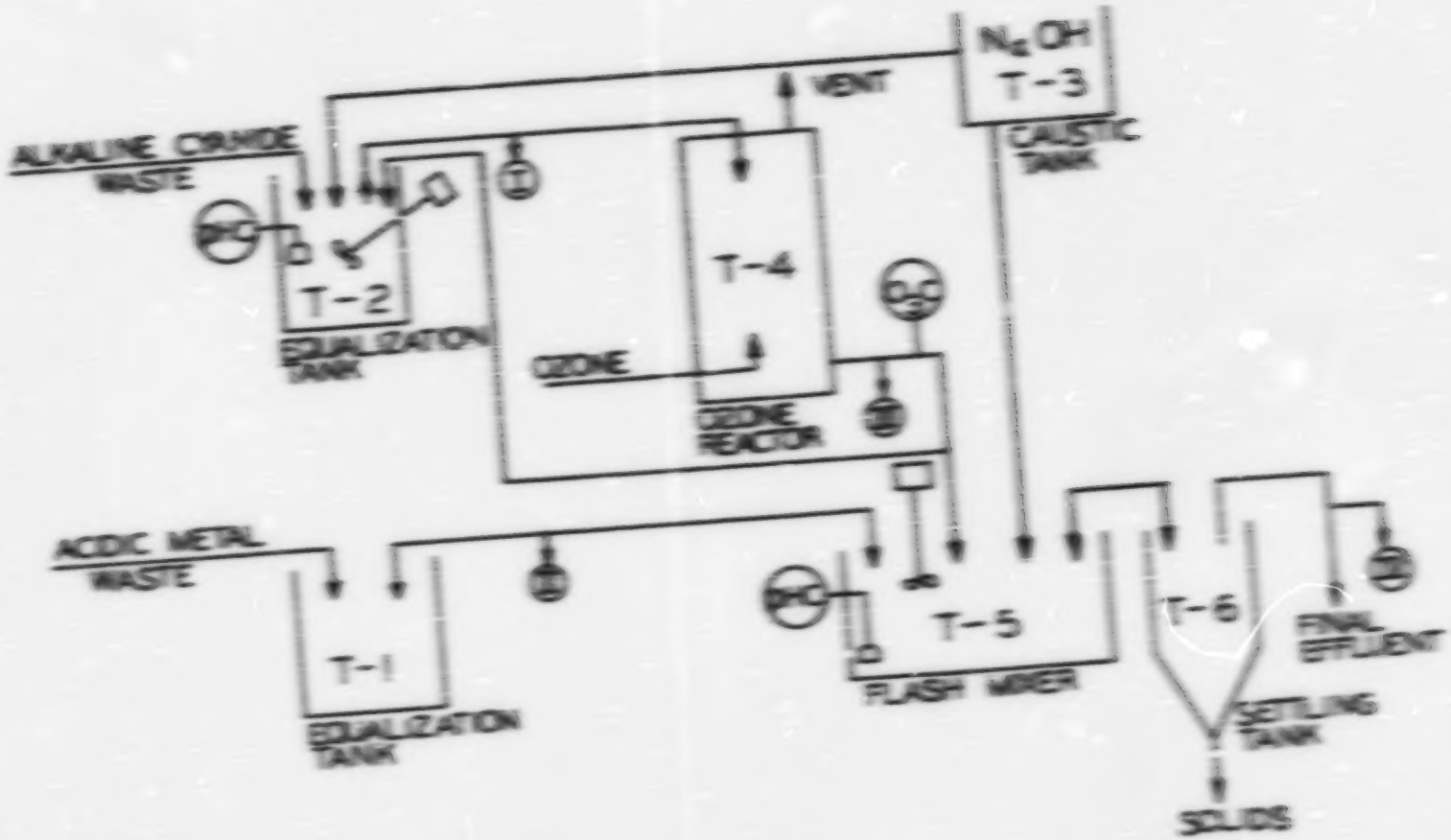

FIG. 1 - FLOW DIAGRAM - SEALECTRO PLATING WASTE TREATMENT PLANT

acid wastewater (T-1). Tank T-2 is provided with a pH sensor, a flash mixer, a pump to transfer wastewater into the ozone reaction tank (T-4), and a water level sensor. The pH of the cyanide wastewater is adjusted automatically in this tank with 15% caustic from a storage tank (T-3).

The acid wastewater is received in Tank T-1. The tank is provided with a water level sensor and a pump (P-1) for the transfer of this wastewater into the flash mixing tank (T-5) where it is combined with ozone-treated alkaline wastewater from the reaction tank (T-4) to gain all possible neutralisation benefit.

The PCI Model G-20-M Ozone Generator has an ozone generating capacity of up to 0.1 kg/day (20 lb/day) of ozone from air under normal operations and up to 12 kg/day (26 lb/day) of ozone using the auxiliary blower. The auxiliary blower is part of the PCI Model PRE-25-M Air Preparation Unit. The air preparation unit provides the clean, oil free, particle free, dry air needed for the generation of ozone. Oxygen could also be used and the output of the same unit would increase twofold.

The ozone reaction tank (T-4) is a fiberglass tank of 2250 l (600 gal) capacity. This tank consists of two major compartments:

The lower, large compartment where the wastewater is treated by ozone. The ozone is introduced through porous diffusers at the bottom of the tank, which is filled with cyanide-containing wastewater.

In the upper, smaller compartment the spent ozone off-gas is reintroduced and either passed through a packed column, sprayed with the incoming cyanide waste or diffused into the incoming cyanide waste. In either mode of operation, this upper compartment serves to remove unreacted ozone from the off-gases to assure complete utilisation of the ozone and to prevent ozone from escaping to the outside atmosphere through the vent.

The fiberglass flash mixer tank (T-5) receives treated alkaline waste from Reaction Tank T-4 and acidic waste from Tank T-1. The combined wastewaters are mixed with the flash mixer and a final pH adjustment then made with caustic or sulfuric acid based on the signal from the pH detector in Tank T-5. The tank is covered to prevent splashing of the wastewater.

The settling tank (T-6) receives the neutralised combined wastewater from the flash mixer tank (T-5). The metal oxides and/or hydroxides settle out in this quiescent tank and the clear, treated water is discharged through the overflow to the sewer. The solid waste is removed manually, as necessary, through a bottom outlet, as a sludge. The calculated retention time in the settling tank is a minimum of 50 minutes.

pH CONTROL SYSTEM

The pH control system consists of the pH detectors mentioned earlier, controllers, and tranducers. All are products of Foxboro Corp. This pH control system adjusts the pH in Tank T-2 and in Tank T-5 by using a 15% caustic

solution held under approximately 52 mm Hg (10 psig) pressure in a pressure rated fiberglass tank (T-3). Compressed air from the PRE-25-M Air Preparation Unit or instrument air from the plant is used to maintain the pressure on the caustic solution in Tank T-3. The caustic solution is fed into Tank T-2 and Tank T-5 as needed through pneumatically controlled metering valves activated by the pH detectors and their automatic controllers. The caustic solution is prepared from caustic flakes in a separate tank (T-3A) and pumped into Tank T-3.

PROCESS CONTROLS

The process controls wired into the central process control unit allow either an automatic mode of operation or manual operation. All major components of this system are fused separately and are wired to permit their operation independently from the total system in the manual mode of operation. The automatic mode of operation makes use of signals from level sensors, located in Tanks T-1 and T-2. Signals from these two level controllers will operate the pumps to transfer cyanide waste into Reaction Tank T-4 or acidic waste into Tank T-5. The wastewaters flow by gravity from these tanks through the rest of the system. The ozone output of the ozone generator is controlled by an ozone detector which assures sufficient ozone for the complete destruction of cyanide in Tank T-4. If there is a wastewater flow through the system, both the ozone generator and the pH control system will operate automatically. A failure of any component, such as a pump or controlling instruments, is indicated by a visual-audio alarm.

The waste treatment plant is separated from the plating facilities and located in a 5.8 m x 5.8 m (19 ft x 19 ft) area with a ceiling height of 4.3 m (14 ft). A removable cover is provided for the portion of the roof directly over the ozone contact tank to permit inside inspection of this tank. The holding tanks (T-1 and T-2) are located underground next to the treatment plant and are accessible through manholes.

LIST OF MAJOR COMPONENTS

Model G-30-M Ozone Generator (PCI Ozone Corp.), with ozone generating capacity of 12 kg/day (26 lb/day) from air (See Figure 2).

Model PRE-25-M Air Preparation Unit (PCI Ozone Corp.), with an output of 0.678 m^3/min (24 scfm), oil free, particle free air with a dew point of -40°C (-40°F) or lower.

Ozone Detector Automatic Controller (PCI Ozone Corp.), one set point unit to maintain an ozone residual of 0.1 to 2.0 mg/l in the effluent from the ozone reaction tank, T-4.

Ozone Reaction Tank (PCI Ozone Corp.) 5.6 m (18.5 ft) tall, 0.8m (30 in) diameter, two compartment fiberglass tank, volume: 2250 l (600 gal), T-4.

Flash Mixer Tank (PCI Ozone Corp.), 1.5 m (5 ft) tall, 0.8 m (30 in)

Figure 1. Anderson Mining Water Treatment Plant.

diameter, fiberglass covered tank, volume: 700 l (180 gal), T-5.

Settling Tank (PCI Ozone Corp.), 2.3 m (7.5 ft) tall, 1.5 m (5 ft) diameter, fiberglass tank with conical bottom, volume: 6600 l (1750 gal), T-6.

pH Detector and Controllers (Foxboro Corp.)

Central Control Panel (PCI Ozone Corp.).

SECTION 5

STUDY OBJECTIVES AND APPROACH

This study was carried out to evaluate the operation of the plating waste treatment plant and to confirm laboratory findings that ozone effectively destroys both cyanide and cyanate and precipitates copper and silver ions as readily settleable solids (6).

Further objectives were to study the effects of changes in major process parameters such as ozone dosage, ozone concentration, pH, and temperature and to find the optimum values for those effects.

Another objective was to establish the cost of this plant and of a new plant based on optimum operating parameters. Both capital cost and operating cost were to be considered.

APPROACH

The study was carried out in three phases as described below. A major constraint placed on the study was that it had to be carried out while the plating plant was in full operation, requiring treatment of plating waste as generated. The plating operation could not be interrupted for extended periods for obvious economic reasons.

In the first phase of the study, the major objective was to learn about the operating characteristics of the plant and to resolve any possible problems, that is, to conduct a plant shakedown operation.

Two problems were encountered during this phase of operation. The first was excessive wastewater flow from the plating plant due both to improper piping that channeled cooling water from air conditioners into the system and due to the simultaneous shakedown operation of the new plating plant and the inexperience of the new crew. The second problem was the presence of significant amounts of cyanide in the acid wastewater line, due again to faulty piping in the plating plant.

During the second phase of the study, the major objectives were to evaluate the effect of process parameters and to determine optimum conditions, while still providing uninterrupted waste treatment for the plating plant.

To accomplish these objectives, the treatment process parameters were varied by upsetting the waste treatment plant's operation temporarily and their effects evaluated as follows:

a) Cyanide concentrations were adjusted by adding concentrated plating solution to the cyanide waste holding tank. The plating plant tended to produce wastewater with a high flow but with low cyanide concentration because of the earlier noted problems. In order to evaluate treatment in the higher (30 to 100 mg/l) cyanide concentration range, plating solution had to be added.

b) Ozone dosage was adjusted upward by increasing the output of ozone or downward by adding concentrated plating solution to the underground cyanide waste holding tank, thereby changing both cyanide concentrations and ozone/cyanide ratio.

c) pH was adjusted in the cyanide holding tank or in the flash mixer and thereby, in the settling tank, independently.

d) The temperature changed naturally as the study progressed through spring, summer, fall, and winter. It did not produce a noticeable effect over the observed range of 14 to 30°C (57 to 86°F).

e) Experimental treatment of sodium cyanide was carried out during a summer plant shut-down of the plating plant to obtain background data.

The temporary large upset of certain process parameters such as cyanide concentration and ozone dosage could only be maintained for about three hours without affecting plating plant operation. Nevertheless, this time was sufficient to obtain useful data from the ozone contact tank; however, equilibrium conditions were not always established in the settling tank. Therefore, metal concentration values obtained for the final effluent under these conditions should be treated with caution. They probably reflect maximum values.

During the third phase of the study, the treatment plant was operated under optimum (or close to optimum) conditions for extended periods to obtain data for process and cost evaluation. These results are compiled and discussed later. Although the plating plant operates within the limits of local and EPA standards for a small plating operation, it produces a large flow of wastewater, far in excess of what would be permitted by the EPA from a large plating operation. In addition, the acid waste flow, which should have contained no cyanide, carried a cyanide concentration of 0.5 to 1.0 mg/l. Scalectro Corp. made repeated attempts to eliminate cyanide from the acid flow by checking piping and floor cracks in the plating plant and by tightening housekeeping operations. As a result, the cyanide concentrations in the acid stream were lowered slightly to 0.2 to 0.8 mg/l. No further improvements were made during the course of the study because of pressing need for production and other economic reasons. Because of the time limitations of this EPA study, the third or final phase of this project was completed under these conditions. The data presented in Section 6 show the results on that basis, as well as residual cyanide analyses of the effluent from the ozone contact tank (T-4). The cyanide concentration in the effluent from the ozone contact tank could consistently be reduced to 0.8 mg/l.

The analyses of the samples were carried out in the laboratories of PCI Ozone Corp. in Stamford, Connecticut* using standard analytical methods described in Table 17. The modified Liebig method was used for all cyanide determinations.

*Presently located in West Caldwell, New Jersey

SECTION 6

OPERATION UNDER OPTIMUM CONDITIONS

Optimum operating conditions were determined by studying the effect of process parameters, as described in Sections 5 and 7.

The optimum process parameters for the Geoelectro Plating Waste Treatment Plant were found to be as follows:

a) Ozone dosage: 1 to 1.5 mole O_3/mole CN^- or 1.65 to 2.8 mg/l O_3 per mg/l CN^-.

b) pH of cyanide waste: 7.0 to 9.5 before ozone treatment.

c) pH of treated final effluent: 8.0 to 8.5 in the settling tank.

d) Ambient temperature any time during the year (14 to 30°C).

The plant was operated under these optimum conditions for approximately two weeks, 16 hours per day, at combined waste flows approximately 1.5 times that of design capacity. Typical data obtained at the extremes of the optimum operating range are shown in Table 5.

The data in Table 4 indicate that an ozone dosage of only one mole of ozone per mole of cyanide ion suffices to reduce the cyanide concentration to 0.08 mg/l in the effluent from the ozone contact tank (Effluent III). However, contamination by CN^- in the acid waste stream caused the final discharge (Effluent IV) to contain 0.64 mg/l cyanide. Metal ion concentrations in the final treated effluent (Effluent IV) were as follows (mg/l):

Copper	1.7
Silver	<0.1 (the limit of detection for the analytical method used.)
Nickel	0.4

The cyanate concentration was 6.0 mg/l. More complete removal of cyanate can be achieved with a higher dosage of ozone, but cyanate control is not necessary to meet local or Federal standards.

These results are remarkably good considering the fact that the acid waste contained 0.2 to 0.8 mg/l cyanide when it was not supposed to contain any. During the treatment sequence the acid wastewater is combined with the ozone treated cyanide waste, the pH adjusted and the combined wastewater fed into the settling tank and then discharged as final treated effluent (IV).

TABLE 3

OZONE TREATMENT OF PLATING WASTE[a]
TYPICAL OPERATING CONDITIONS

Experiment		A	B
Cyanide Waste Input			
CN^- @ Port I	(mg/l)	15.2	12.9
Ozone	(mg/l)	29.7	35.2
$(O_3)/(CN^-)$		1.05	1.48
$(O_3\text{-Cu})/(CN^-)$[b]		1.05	1.47
pH at Sample Ports[c]			
CN Tank (I)		7.0-8.0	9.5
Reactor (III)		7.0	7.0-8.0
Clarifier (IV)		9.5	9.0
Metal Input in Combined Inflow (I + II)			
Cu	(mg/l)	4.24	7.50
Ag	(mg/l)	NF[d]	0.71
Ni	(mg/l)	0.84	NF
Effluent from Ozone Treatment Tank (III)[e]			
CN^-	(mg/l)	0.08	0.08
CN Removal	(%)	99.5	99.4
Final Effluent (IV)[f]			
CN^-	(mg/l)	0.04	0.85
CNO^-	(mg/l)	6.0	4.2
Cu	(mg/l)	1.7	2.2
Ag	(mg/l)	B	B
Ni	(mg/l)	0.4	0.7

[a] Plating Waste: $Na_3Cu(CN)_4$ at 34 l/min (9 gpm) flow, 1.33X design flow of 25.5 l/min (6.75 gpm). Acidic waste flow: 94.5 l/min (25 gpm) at 1.5 X design flow of 60 l/min (16 gpm).

[b] $(O_3\text{-Cu})/(CN^-)$ is the mole ratio after accounting for oxidation of Cu^+ to Cu^{++}.

[c] Roman numerals refer to sampling ports indicated on Figure 1.

[d] NF = None Found.

[e] Ozone treated cyanide waste before mixing with acid waste.

[f] Metal values = total; includes soluble plus suspended.

[g] Detected at limit of detection of procedure used, 0.1 mg/l for Ag.

Cyanide in the acid waste stream has two undesirable effects. It increases the cyanide concentration in the effluent. That is the reason why Effluent III contains only 0.08 mg/l cyanide while Effluent IV contains 0.64 mg/l. The second undesirable effect is that the cyanide present in the settling tank may increase the solubility of metal ions by complexing. The system is so designed that the acid waste cannot be segregated. Correction lies in improved maintenance and housekeeping. Nevertheless, even with this minor problem, the Scalectro Plating Waste Treatment Plant meets all local and EPA code requirements, as discussed in Section 1. Cyanide concentration was consistently reduced to 0.08 mg/l in the ozone reactor effluent.

Another key point worth mentioning is that repeated measurements, using a Mast ozone meter, showed no significant ozone emission in the vent gases from the ozone contact tank. All measurements showed an ozone concentration of 0.05 ppm or less.

The sludge from the settling tank was collected during the two weeks of optimum conditions operation. A very small amount of sludge formed during that time (approximately 1 to 2 kg on a dry basis). It was readily settleable and filterable. A sample was dried at 130°C and analyzed for metal content, using atomic absorption spectroscopy. The results are as follows: copper 18%, silver 0.1%, nickel 18%, iron 0.6%, lead 0.8%, tin 24%, all by weight.

SECTION 7

STUDY OF PROCESS PARAMETERS

The effect of various process parameters on the plating waste treatment was studied to establish optimum operating conditions. The study was carried out by temporarily upsetting the various parameters and recording their effect without interrupting the operation of the treatment plant or of the plating facility. This approach permitted the normal production schedule for the plating plant to be maintained.

The study could not be made as detailed and thorough as would have been preferred due to time and budget limitations. An added limitation was the initial operating difficulties with the new plating plant and the inexperience of the operating personnel with the new equipment.

The approach used for the study was discussed in detail in Section 5. The quality of the final treated effluent was somewhat affected by low cyanide and metal concentrations in the acid waste as noted in Section 5 and 6.

The results of the process parameter study are compiled in Tables 4, 5, 6 and 7. The data in these tables include most of the information obtained when the treatment plant was operated under upset operating conditions, with less than stoichiometric amounts of ozone and with both a small excess and with a large excess of ozone. For ease in understanding, these data are also presented in a summarized form in Tables 8, 9, 10 and 11 later in the report, together with the following discussion of the various process parameters.

The effect of ozone dosage or the ozone/cyanide mole ratio was studied at several concentration levels of cyanide. These studies showed that ozone dosage is the most important process parameter. The results are as follows:

a) At a low cyanide concentration (to 20 mg/l) an O_3/CN^- mole ratio of 1:1 is sufficient to reduce cyanide concentrations to below 0.1 mg/l, as indicated by the data in Table 8;

b) At intermediate cyanide concentrations (20 to 40 mg/l) a mole ratio of 2.0 ozone/cyanide is needed to reduce the cyanide concentration to $\leq$1 mg/l and 3.6 to achieve $\leq$ 0.1 mg/l, as indicated by the data in Table 9. The relationship for cyanate is less clear, but suggests that high O_3/CN^- ratios (3.6) are also necessary for effective destruction;

c) At higher concentrations ($\geq$50 mg/l) a mole ratio of 1.33 ozone/cyanide reduces the cyanide concentration to 0.52 mg/l, as indicated by the data in Table 10. This ratio is inadequate for effective CNO$^-$ removal.

TABLE 5

OZONE TREATMENT OF PLATING WASTE
LESS THAN STOICHIOMETRIC OZONE DOSAGE[a]

Experiment No.		1	2	3	4
Cyanide Waste Input					
CN^- @ Port I	(mg/l)	71.0	75.0	75.0	75.0
Ozone	(mg/l)	46.0	50.5	48.0	48.0
Mole Ratio (O_3/CN)		0.35	0.35	0.35	0.35
pH At Sample Ports[b]					
CN^- (I)		8.5	8.6	8.1	9.4
Reactor (III)		8.1	8.1	8.0	9.1
Clarifier (IV)		8.5	9.5	7.1	6.6
Metals in Combined Inflow (I) + (II) (mg/l)					
Cu		20.7	21.0	28.2	26.6
Ag		0.71	0.45	0.24	NF
Pb		NF[c]	1.1	NF	0.6
Ni		1.4	NF	NF	NF
Sn		NF	NF	NF	NF
Ozone Reactor Effluent (III) (mg/l)					
CN^-		12.1	5.4	12.8	11.5
CNO^-		48.0	65.0	25.0	47.0
Final Effluent (IV) (mg/l)[d]					
CN^-		5.2	1.8	4.2	5.6
CNO^-		5.5	4.6	0.0	0.0
Cu		8.1	10.3	22.4	11.9
Ag		1.03	0.46	0.14	0.17
Pb		NF	NF	NF	NF
Ni		1.41	NF	0.89	0.62
Sn		NF	NF	NF	NF
Percent Removal at (IV)					
CN^- (%)		95.5	97.6	94.4	93.9
CNO^- (%)		94.8	93.7	100.0	100.0

[a] Cyanide Complex, $Na_2Cu(CN)_4$ plating work at 34 l/min (9 gpm) flow, 1.33X design flow of 25.5 l/min (6.75 gpm). The acidic waste flow was 94.5 mg/l (25 gpm), 1.5 X design flow of 60 l/min (16 gpm). The ozone concentration represents the amount of ozone fed into the reactor.

[b] Roman numerals represent sample ports as per Figure 1.

[c] NF - None Found.

[d] The metal analyses at IV should be considered only as an indication because sufficient time probably was not allowed for the clarifier to reach equilibrium.

Table 6

[illegible]

Inlet			[illegible]			Reactor Effluent (ET)			Final Effluent (EF)			
COD_{Cr} @ 1 hr (mg/l)	Phenol (mg/l)	Ratio Biodeg. (BOD_5/COD_{Cr})	COD_{Cr} (I)	Reactor (II)	Centrifuge (III)	COD_{Cr} (mg/l)	COD_{Cr}	COD_{Cr} % Removal	COD_{Cr} (mg/l)	COD_{Cr}	COD_{Cr} % Removal	COD_{Cr}
15.2	28.7	1.85	7.1-8.0	7.0	12.0	—	—	—	0.64	6.0	96.6	40.5
62.0	172.1	1.55	12.0	10.0	6.0	2.32	42.5	96.2	0.90	6.4	98.6	96.7
38.0	109.0	1.84	10.2	8.9	6.5	4.23	33.6	96.1	0.60	6.3	98.4	95.4
57.5	74.0	2.02	10.9	9.0	6.5	4.35	8.9	96.1	0.9	4.4	97.6	88.3
36.2	104.6	1.91	11.2	9.0	9.0	0.21	7.2	99.4	0.75	6.5	97.9	95.6
26.0	104.0	2.04	10.6	8.7	6.9	0.28	6.0	98.7	0.31	6.9	98.9	100.0

[illegible] BOD_5.

[illegible] as per Figure 1.

TABLE II

THE EFFECT OF OZONE DOSAGE AT LOW CONCENTRATIONS OF CYANIDE[a]

Influent Cyanide Ion mg/(l)	Mole Ratio (O_3:CN^-)	pH at (I)	Ozone Reactor Effluent (II) (CN^- mg/l)
2.1	11.57	8.0	0.06
5.3	6.62	12.6	0.04
6.5	5.39	10.1	0.06
12.9	1.46	7.5	0.06
13.0	2.49	7.7	0.02
15.2	1.85	9.5	0.08

[a] Cyanide is present as $Na_2Zn(CN)_4$.

[illegible]

[illegible]

[illegible]

TABLE II

THE EFFECT OF CYANIDE CONCENTRATION
AT CONSTANT OZONE TO COPPER CYANIDE RATIOS[a]

Cyanide Ion (Mg/L)	Mole Ratio (O_3/CN^-)	pH at (I)	Ozone Reactor Effluent (III) Conc. (Mg/L)		% Removal	
			(CN^-)	(CNO^-)	(CN^-)	(CNO^-)
37.5	0.35-0.5	10.9	0.55	3.9	98.1	76.5
75.0	0.35-0.5	9.4	11.5	47.0	84.6	37.3
12.9	1.3 -1.6	9.5	0.08	4.2	99.4	----
65.0	1.3 -1.6	11.0	0.52	42.5	19.2	----
15.0	2.3 -2.7	7.7	0.02	ND[b]	----	----
52.0	2.3 -2.7	11.0	0.38	15.0	98.8	59.4
34.2	2.3 -2.7	9.6	0.6	ND	98.2	ND

[a] Cyanide is present as $Na_2Cu(CN)_4$
[b] None detected

insufficient experimentation was done at this level, which is well beyond that encountered by Sealectro, to arrive at more specific conclusions such as the ozone dosage needed for complete CN^- removal ($\ll$0.1 mg/l).

d) The effect of cyanide concentration at three ozone/cyanide ratios is shown in Table 11. These data again suggest that a larger dosage of ozone is needed to reach the same residual cyanide concentration ($\ll$1 mg/l) at higher influent cyanide concentrations.

The pH of the cyanide waste prior to ozone treatment (Sample Port I) was found not to be a critical variable in the range of 7.0 to 13.0, as shown by data in Table 7. It was observed that ozone treatment lowers the pH by approximately one pH unit, as indicated by comparing the data in Tables 4, 6 and 7, for Sample Ports I and III, i.e., before and after ozonation.

The pH of the treated effluent in the clarifier also is not critical, as far as the cyanide and cyanate concentrations are concerned. Acidic pH in the settling tank leads to lower cyanate and cyanide concentrations probably by accelerating decomposition of them as indicated by the data in Table 4. Surprisingly, the acidic pH did not seem to increase the total copper and silver concentrations in the effluent (IV). The explanation may be that these metals are present as relatively insoluble oxides or the times of these experimental runs were insufficient to establish equilibrium in the settling tank (See Section 5). Analyses are, however, total values and it should be noted that the metal values presented in Tables 4 to 7 reflect both soluble and suspended (non-settled) metal in the effluent.

An increase of ozone concentration from 1% to 2% in the ozone feed did not produce a significant reduction in cyanide or cyanate concentration under the test conditions, as indicated by the data in Tables 4 and 7. This result suggests that mass transfer of ozone is not the limiting parameter under the conditions of this study.

The reaction temperature was carefully recorded for all experiments but variations did not produce an observable effect. No effort was made to control the temperature. The ambient wastewater temperature varied in the range of 14 to 30°C during the test program.

SECTION 8

TREATMENT OF SODIUM CYANIDE

The ozone treatment of sodium cyanide was studied during a summer plant shut-down. The approach taken was as outlined in Section 5. The results summarized in Table 12 indicate that ozone treatment effectively destroys sodium cyanide as well as the cyanate generated as an intermediate. Complete removal of cyanide and cyanate is possible if a sufficiently large ozone dosage is used. A mole ratio of 2.65 ozone/cyanide or higher removed at least 97.6% of the cyanide. However, a mole ratio of 4.3 ozone/cyanide was needed to remove 44.8% of the cyanate generated and an O_3/CN^- ratio of 14.0 was needed for 97% CNO^- removal. The pH was again not critical based on reactions carried out at several pH's in the range of 7.7 to 10.5. Thus, it appears that ozonation of cyanide is more rapid than the ozonation and, possibly, the hydrolysis of cyanate.

The main process parameters, cyanide concentration, ozone/cyanide mole ratios, and pH were varied through a very broad range to cover all areas of interest. Additional experiments are still needed to refine the results.

TABLE 12

OZONE TREATMENT OF SODIUM CYANIDE ON PLANT SCALE[a]

Influent Cyanide Ion (mg/l)	Influent Mole Ratio (O_3/CN^-)	pH at Sample Points[b] I	pH at Sample Points[b] III	Ozone Reactor Effluent (III) Conc. (mg/l) (CN^-)	Ozone Reactor Effluent (III) Conc. (mg/l) (CNO^-)	% Removal (CN^-)	% Removal (CNO^-)
5.6	45.0	8.2	5.4	0.0	0.0	100.0	100.0
19.2	14.0	7.7	5.7	0.23	0.6	98.8	96.9
38.0	8.11	8.2	5.4	0.23	5.3	98.7	78.6
94.0	4.32	9.6	7.5	0.38	30.0	98.9	44.8
55.0	2.46	10.1	8.9	1.30	56.0	97.6	36.5
140.0	1.54	10.5	9.6	40.0	71.0	71.4	37.5
250.0	0.58	10.4	9.2	71.0	200.0	71.6	28.2

[a] Sodium Cyanide (NaCN)

[b] Roman numerals represent sample ports as per Figure 1

SECTION 9

DISCUSSION

This demonstration study program reconfirmed on a plant scale our earlier laboratory findings (6) that ozone treatment of copper cyanide plating waste is effective, economical, safe and reliable. The treatment of sodium cyanide is also effective. It was studied briefly in order to establish relative ease of treatment on a plant scale. The data in Tables 5 and 11 indicate that copper cyanide reacts faster and requires less ozone than does sodium cyanide. This is consistent with earlier evidence that copper is a catalyst for cyanide ozonation.

The Sealectro Plating Plant is a small plating facility. It plates approximately 2.0m^2/hr surface area and has an installed DC amperage capacity of 1200 amps. The wastewater discharge from this plant is subject to the Westchester County Sewer Code and the EPA standards for small plating installations, as discussed in detail in Section 3. The Sealectro Plant operates well within those standards when following the standard operating procedures with the PCI ozone system.

The new Sealectro Plating Plant produces an average flow of 130 l/min (34 gpm) wastewater consisting of 34 l/min (9 gpm) alkaline cyanide flow and 95 l/min (25 gpm) acid waste flow. This is an unusually high flow for such a small operation. The management believes that the high rinse water flow assures the all important high quality plating at minimum cost. Furthermore, the acid flow should contain no cyanide, but it does contain cyanide in the range of 0.2 to 0.8 mg/l from leaks and unidentified sources.

The above two problems, namely excessive wastewater flow and cyanide in the acid line, placed a limitation on this study. Efforts were made by Sealectro Corp. to resolve them. Definite improvements were made, but the problems were not completely resolved during this study. We expect that with further experience in the plating shop these problems will be minimized and resolved.

The demonstration study produced valuable information concerning the process parameters for plating waste treatment and the safety of ozone treatment, as discussed below. It should be recognized that the data obtained in this study are strictly true for the ozone contactors used and for ozone contactors of very similar design. Other type of contactors such as multistage diffusion systems, positive pressure injectors, etc., may lead to somewhat different results. Key considerations should be the mass transfer rate of ozone and the concentration of cyanide being treated.

OZONE DOSAGE

The ozone dosage, that is, the mole ratio of ozone to cyanide, is the most important process parameter. However, the ozone dosage required for the complete destruction of cyanide is also dependent on the cyanide concentration. A mole ratio of 1 to 1.5 mole ozone per mole of cyanide was found to be sufficient for the complete destruction ($CN^- \leq 0.1$ mg/l) of copper cyanide when cyanide concentration was 20 mg/l or less. This requirement gradually increases to 3.0 moles of ozone per mole of cyanide at cyanide concentrations of 75 mg/l.

There are several possible explanations for the dependence of the mole ratio on cyanide concentration, as follows:

a) The mass transfer of ozone from gas to water is the rate controlling step in the initial stages of the reaction. The destruction of the last 4 to 5% cyanide is reaction rate controlled (10). To achieve complete cyanide destruction (0.1 mg/l CN^- or less) at high initial cyanide concentrations, ozone must be fed into the system for a longer period of time under slow, reaction rate controlled conditions. However, under these conditions more ozone may be consumed by competing side reactions such as oxidative destruction of cyanates to carbon dioxide.

b) The cyanide waste may also contain hard-to-decompose cyanide complexes such as iron complexes or slower reacting sodium cyanide. These require a higher mole ratio of ozone to lower the final level of cyanide to 0.1 mg/l or below. Although we have occasionally detected iron in the Sealectro plating waste, in most cases it was not present in significant amounts. The waste was not analyzed for other cyanide salts or complexes.

c) The final, reaction rate controlled part of the reaction may be slow because all the copper is removed by oxidation and precipitation as insoluble copper oxide; thus, no copper catalysis occurs.

Most likely all three cases occur. However, the Sealectro Plant normally treats a relatively low concentration of cyanide where these problems are not very important. At higher cyanide concentration, the ozone dosage might be minimized by using a multistage ozone contact tank with possible uv irradiation in the final stage, if necessary.

pH OF CYANIDE WASTE

The pH of cyanide waste before the ozone treatment is relatively unimportant in the range of 7 to 10. Since the cyanide waste is normally discharged from the plating plant in this pH range, no pH adjustment is necessary prior to ozone treatment. This finding represents a significant saving in capital cost since it eliminates one complete pH control system and one agitator.

REACTION TEMPERATURE

Reaction temperature did not have a significant effect in the normal ambient temperature range of 14 to 20°C, which is in agreement with previous observations (12).

SLUDGE FROM THE REACTION

The sludge from the reaction was collected at the bottom of the clarifier. The sludge that settled during the process parameter study was discarded, since there was no way to assure equilibrium conditions in the settling tank.

During the optimum conditions experiments the sludge was collected. However, only a small amount formed during the two weeks of operation. The sludge was heavy, readily settleable, and filterable. The analysis of its metal content is noted in Section 6. The operation of the settling tanks was not studied in depth due to the shortness of the study time. The use of coagulants and settling tubes could be expected to improve the settling substantially and could result in further improvements in the effluent quality.

RECYCLING OF TREATED EFFLUENT

Recycling of treated effluent was outside the scope of the project and was not investigated due to a lack of time. However, it is clear that the effluent could be used as cooling water for the ozone generator and for other equipment, such as air conditioning and other machinery.

The recycling of the effluent into the plating process is a real possibility in the Sealectro Plant under the following conditions:

a) If cyanide is kept out of the acid waste flow.

b) If a slightly larger ozone dosage is used, approximately 2 moles of ozone per mole of cyanide, to assure essentially complete removal of all cyanate and copper and, possibly, more of the other trace metals.

c) If a coagulant is added or settling tubes are used in the settling tank to further improve metal removal.

Naturally, prior to embarking on a recycling program it should be ascertained that there is no adverse effect on plating quality.

In conclusion, the Sealectro demonstration project is believed to have achieved its major objectives and is presently discharging an environmentally acceptable effluent.

SECTION 10

COST EVALUATION

The Sealectro Plating Waste Treatment Plant was designed with the requirements of a plant demonstration study in mind. Consequently, the design exceeds the normal requirements for an operating plant in several respects, especially in ozone generating capacity, instrumentation and flexibility built into the plant. Naturally, these extras carry a price tag. Therefore, the cost data given here should be considered with the above in mind.

To present the most accurate and useful cost evaluation, data are compiled for the Sealectro Plant as it was built, as well as for a new hypothetical plant as it would be built as an optimized operating plant based on the Sealectro experience. The Sealectro data were based on 1973 prices while the new plant data are based on 1975 prices.

The Sealectro Plant proved by weeks of continuous (16 hr/day) operation that it can treat the following plating waste, well above original design values:

a) Cyanide Waste: 34 l/min average, 57 l/min peak (9 gpm average, 15 gpm peak) for short periods, cyanide (CN^-) concentration ≤ 60 mg/l.

b) Acid Waste: 95 l/min average, 130 l/min peak (25 gpm average, 35 gpm peak) for short periods.

c) Total Combined Flow: 134 l/min average, 190 l/min peak (34 gpm average, 50 gpm peak) for short periods.

The cost data summarized in Tables 13 to 16 are based on a 24 hr/day, 5 day/week operation for the optimum plant and a 16 hr/day, 5 day/week operation for the Sealectro Plant.

The total operating plus capital cost of treating the plating waste is $0.35/1000 l ($1.31/1000 gal) and $0.59/1000 l ($2.24/1000 gal) for the optimum plant and the Sealectro Plant, respectively. These figures are based on 15 year straight line depreciation.

The optimum system achieves certain savings made possible on the basis of this first demonstration project and excludes certain costs incurred in the Sealectro Plant to allow more complete evaluation during the study.

TABLE 15

CAPITAL COST OF OZONE TREATMENT

		1975 Optimum	1974 Actual
Ozone Generator, PCI, G-30 with auxiliary Air Prep Unit PRS-25	30 lb/day O_3	$25,000	$ -
	25 lb/day O_3	-	36,000[a]
Ozone Detector - Auto Control - PCI		2,700	2,500
Tanks		3,000	3,900
pH Control System - Foxboro/PCI		3,000	2,800[b]
Installation		5,000	10,000
Central Control Panel		-	600
Building	300 sq ft @ $25/ft^2	7,500	-
	360 sq ft @ $22/ft^2	-	7,933[c]
Holding Tanks, pumps, auxiliaries	(above ground)	5,000	-
	(underground)	-	12,691[d]
	TOTAL CAPITAL COST	$51,200	$66,613

a The ozone generating capacity of this ozone generator is 30% higher than necessary to provide flexibility for the EPA study.

b Although only one pH control loop is necessary, two loops were installed to provide flexibility for the EPA study.

c The cost of the building may vary depending on location and type of construction.

d The holding tanks at Realectro were exceptionally expensive. Due to space limitations they were installed underground in a high water table, flood area. Normally, above ground tanks would suffice.

TABLE 14

WEEKLY OPERATING COST FOR OZONE TREATMENT

		1975 Optimum	1973 Actual[a]
Labor:	caustic make-up, operate 5 hr/wk @ $10/hr	$ 50.00	
	5 hr/wk @ $10.67/hr	-	$ 50.01
Maintenance:	maintenance, repair, housekeeping 5 hr/wk @ $7/hr	35.00	-
	7 hr/wk @ $5.52/hr	-	38.64
Power	20 lb O_3/day @ 11.5 kwh/lb O_3 @ 5¢/kwh	57.50[b]	
	10 lb O_3/day @ 11.5 kwh/lb O_3 @ 7¢/kwh	-	26.83
Chemicals	420 lb NaOH/wk @ 26¢/lb	109.20	
	600 lb NaOH/wk @ 27¢/lb	-	162.00
	TOTAL OPERATING COSTS	$251.70	$277.48
	OPERATING COST/DAY	50.34	55.50

[a] These were the actual operating costs based on 16 hr/day operation.

[b] Anticipated power cost for the optimum plant is higher because a higher CN^- concentration (60 mg/l) is assumed. In the actual Sealectro plant CN^- concentration was less than half this value.

TABLE 15

TREATMENT COSTS

	1975 Optimum 24 hr/day	1973 Actual 16 hr/day[a]
Capital Cost $	51,200.00[b]	66,613.00[b]
$/1000 gal	1,048.70[b]	2,040.86[b]
$/1000 l	276.76[b]	539.91[b]
Total Operating Cost $/day	50.54	55.50
$/1000 gal	1.03	1.70
$/1000 l	0.27	0.45
Total Treatment Cost $/day[c]	69.09	75.26
$/1000 gal	1.51	2.24
$/1000 l	0.55	0.59

[a] Due to the 16 hr/day operation at Sealectro, these costs are approximately 1.5% higher than they would be for a 24 hr/day operation.

[b] These costs are capital cost/daily volume and not depreciated.

[c] These costs include capital equipment depreciated over 15 years (at 250 day/yr) and operating costs.

TABLE 16

CYANIDE DESTRUCTION COSTS

	1975 Optimum 24 hr/day	1975 Actual 16 hr/day[a]
Capital Cost		
$/day	45,000.00[b]	55,455.00[b]
$/1000 l	918.58[b]	1,698.41[b]
$/1000 gal	3,473.22[b]	6,420.00[b]
$/kg CN	15,254.25[b]	28,182.55[b]
$/lb CN	6,933.74[b]	12,810.25[b]
Operating Cost		
$/day	18.50	15.09
$/1000 l	0.38	0.46
$/1000 gal	1.43	1.75
$/kg CN	6.27	7.66
$/lb CN	2.85	3.48
Total CN Removal Costs[c]		
$/day	30.50	29.88
$/1000 l	0.62	0.91
$/1000 gal	2.35	3.45
$/kg CN	10.34	15.18
$/lb CN	4.70	6.90

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a Due to the 16 hr/day operation at Sealectro, these costs are approximately 1.5X higher than they would be for a 24 hr/day operation.

b These costs are not depreciated.

c These costs include capital equipment depreciated over 15 years (at 250 day/yr) and operating costs.

SECTION 11

ANALYTICAL METHODS

Table 17 presents the references for the analytical procedures used during the course of this project. These are the methods commonly used in the electroplating industry, although it must be recognized that only the larger companies can be expected to have the equipment and trained personnel necessary to carry out the analyses. (It should also be noted that analytical services, either in-house or purchased, were not included as a line item in the cost assessment.)

TABLE 17

ANALYTICAL METHODS

Compound to Be Analyzed	Method Used	Range of Application (mg/l)	Limit of Detection (mg/l)	Source
NaCN as CN*	Modified Liebig Titration	1-20	0.1	a
$Na_2Cu(CN)_4$ as CN	Modified Liebig Titration p-dimethylben-salrhodanine as indicator	1-20	0.1	a
"	Pyridine-Pyrazolone Colormetric	0.07-5	0.05	b
"	Selective Ion Electrode	1.0 -10.0	0.5	c, d
CNO*	Modified Nessler Method	1.0 -10.0	0.5	a
Cu	Atomic Absorption Spectroscopy (A.A.S.)	0.2	0.2	f
Ag	"	0.1	0.1	f
Ni	"	0.3	0.3	f
Pb	"	0.5	0.5	f
Sn	"	20	20	f

Sources

[a] Dodge, Zabban & Serfass, Analytical Methods for the Determination of Cyanides in Plating Wastes and in Effluents from Treatment Processes, Plating, 39: pp 267-273, 1952.

[b] Standard Methods for the Examination of Water and Wastewater, APHA: AWWA: WPCF, 1965, pp. 448-457.

[c] Riseman, John, Electrode Techniques for Measuring Cyanide in Wastewaters, American Laboratory, Dec. 1972.

TABLE 17 (Continued)

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[g] Instruments used for analysis: 1. Beckman Spectrograph Model DB-GT. 2. A.A.S. - Atomic Absorption Spectrophotometer made by Astec, Inc. 3. Selective Ion Electrode, Model 407A, Orion Corp. (CN^-) electrode 94-06A; Ref electrode 91-0100.

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